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Vibrational analysis of hydroxyacetone

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Abstract

In order to be able to fully understand the vibrational dynamics of monosaccharide sugars, we started with hydroxyacetone $\text{CH}_2\text{OHCOCH}_3$, and glycolaldehyde CH_2OHCOH , which are among the smallest molecules that contain hydroxyl and carbonyl group on neighboring carbon atoms. This sterical configuration is characteristic for saccharides and determines their biochemical activity. In this work vibrational analysis of hydroxyacetone was undertaken by performing the normal coordinate analysis for glycolaldehyde first, and transferring these force constants to hydroxyacetone. The observed Raman and infrared bands for 90 wt.% solution of hydroxyacetone in water (acetol) were used as a first approximation for the bands of free hydroxyacetone. The number of observed Raman and infrared bands for acetol exceeds the number of calculated values for the most stable hydroxyacetone conformer with C_s symmetry, which suggests more than one conformer of hydroxyacetone in water solution. In particular, there are two bands both in infrared (1083 and 1057 cm^{-1}) and in Raman spectrum (1086.5 and 1053 cm^{-1}) that are assigned to the CO stretching mode and this is one of the indicators of several hydroxyacetone conformers in the solution. Additional information was obtained from low temperature Raman spectra: at 240 K a broad asymmetric band centered around 280 cm^{-1} appears, suggesting a disorder in the orientation of hydroxyl groups. Glassy state forms at ~ 150 K. The broad band at 80 cm^{-1} is assigned to frozen torsions of hydroxymethyl groups.

PACS

31.50 Bc; 33.15 Bh; 33.20 Ea; 33.20 Fb

1. Introduction

Our knowledge of cellular molecular organization has advanced rapidly in recent years [1] and [2]. In particular, carbohydrates gained on significance since not only they serve as energy storage, participate in the building of DNA and RNA and are structural elements in plants' cell walls [3], but also bind with proteins to form glycoproteins and proteoglycans and thus influence cell growth and maturization of specialized tissue. They also form sophisticated extracellular matrices throughout the organism [4] and [5].

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Glycolaldehyde together with smaller sugars is produced at the initial stages of nonenzymatic glycosylation of proteins, the pathological reaction which produces cross-linking and disables proteins' biological function [6]. It is known that the advanced glycation end products (AGEs) agglomerate in the tissue affected by *Diabetes mellitus*, such as in eye lens [7] and [8].

Common to all monosaccharides, be they aldehydes or ketones, is the occurrence of carbonyl group next to hydroxyl group in the chain conformation of sugar molecule. Since the behavior of these hydroxy-carbonyl compounds in water is extremely complex (for glycolaldehyde and glyceraldehyde see [9], [10] and [11]), vibrational analysis of solutions cannot be reliable unless the spectral database of the participating chemical species is complete. As a first step glycolaldehyde CH_2OHCOH , and hydroxyacetone $\text{CH}_2\text{OHCOCH}_3$ were chosen for study.

Glycolaldehyde at room temperature appears in the form of a dimer (2,5-dihydroxy-1,4-dioxane) which crystalizes in a mixture of two phases, α and β , as found by Kobayashi et al. [12]. The symmetry of these crystal phases as well as molecular conformation in each of them has not been determined yet by X ray crystallography, but the infrared and Raman study of Kobayashi et al. [12] suggests the *trans* axial position of two OH groups in the phase α , and their equatorial position in the phase β . Previous research on glycolaldehyde that employed vibrational spectroscopy includes the work of Michelsen and Klaboe [13], infrared matrix isolation study of Aspiala et al. [14], and, more recently, Yaylayan et al. studied transformation of glycolaldehyde with temperature and in different solvents [15]. Quite a few ^1H NMR studies were done on glycolaldehyde [9], [10], [11], [16], [17], [18] and [19] and one on hydroxyacetone in aqueous solutions [20]. Whereas glycolaldehyde exhibits really complicated behavior in water, methanol and dimethyl sulphoxide, forming several types of open and closed dimers, as well as hydrate and enediol [10] and [15], hydroxyacetone in water seems to remain a monomer [20]. Both free glycolaldehyde [21] and [22] and hydroxyacetone [23] exhibit intramolecular hydrogen bonding that establishes planar $\text{C} - \text{O} \dots \text{HO} - \text{C}$ conformation as the energetically most favorable.

Since there were some discrepancies in the vibrational assignment of the glycolaldehyde bands and no assignment has been done for hydroxyacetone so far, semi-empirical normal coordinate analysis was performed with valence force constants transferred from well established force fields of acetone and acetaldehyde [24] and ethylene glycol [25], with very few modifications. The purpose of this calculation in the harmonic approximation was to identify the hydroxyacetone bands most sensitive to hydrogen bonding and conformation of the molecule by comparing the calculated bands positions with the observed Raman and infrared bands of water solution of hydroxyacetone (acetol).

2. Experimental

Raman spectra of liquid acetol in an open glass cuvette were obtained with DILOR Z24 triple monochromator operating in sequential mode, in standard 90° geometry. The step was 1 cm^{-1} ,

the slitwidth was 300 μm , time constant 1 s, and the accuracy of the observed bands positions better than 1 cm^{-1} . The COHERENT INNOVA 100 argon ion laser operating at 514.5 nm with the laser power of 200 mW served as an excitation source. Low temperature Raman spectra of acetol were obtained while the sample, sealed under vacuum in the capillary tube, was cooled down with CTI CRYOGENICS closed cycle helium cryostat with Lake Shore controller.

Infrared spectra were recorded on Perkin Elmer 2000 instrument, with 20 scans and the resolution of 1 cm^{-1} using Perkin Elmer liquid cell with KBr windows.

Commercial acetol (90 wt.% solution of hydroxyacetone in water) was purchased from Sigma-Aldrich and used without further purification. The substance turned out to be very hygroscopic, and water absorption from the air very pronounced. Therefore in several occasions we used the stream of hot air to evaporate the water from the solution, notifying the spectral changes. The temperature to which the sample was warmed up is estimated to be $\sim 50\text{ }^{\circ}\text{C}$, which is much less than the boiling point of acetol ($145\text{ }^{\circ}\text{C}$ from manufacturer's data). The vapour pressure at room temperature is estimated to be less than 0.5 kPa. An attempt to record Raman spectrum of vapour failed due to water condensation on windows of quartz Raman cell during the heating of solution.

Vibrational frequencies were calculated in harmonic approximation using program package of Schachtschneider [26].

3. Results

Although having similar chemical composition, glycolaldehyde and hydroxyacetone have rather different equipotential energy surface judging by the ones calculated by ab initio methods [14], [27] and [28]. We define as τ_1 the CH_2O torsional angle around $\text{C}_1\text{--C}_2$ bond, and as τ_2 the OH torsional angle around $\text{C}_1 - \text{O}_3$ bond. In the notation of reference [14] we denote *cis* conformation with respect to τ_1 with big letter **C**, and *cis* conformation with respect to τ_2 with small letter **c**. In the same manner *trans* conformers are denoted with **T** and **t**. For both molecules the most stable conformer is the one where hydroxyl and carbonyl group are in *cis* position (as shown in Fig. 4 and Fig. 5), or **Cc**. Quantum calculations on glycolaldehyde predict that the next stable conformer **Tt** has ~ 10 [14] or 14 kJ mol^{-1} [27] higher energy than **Cc** conformer. For hydroxyacetone the minimum of the **Cc** conformer is even deeper—the next stable conformation lies at least 90 kJ mol^{-1} higher [28].

Polarized Raman spectra of acetol are shown in Fig. 1 and Fig. 2. In Fig. 3 the infrared and Raman spectrum of the acetol previously heated for 15 min in the stream of hot air are compared. This warming up turned out to be a necessity for obtaining a good quality infrared spectrum since the sample sorbes water from the air rather quickly. Two spectral differences were noted in the Raman spectrum on heating: the band at 2854 cm^{-1} shifts to lower wavenumbers, and a

shoulder at 1053 cm^{-1} becomes a pronounced band at 1028.5 cm^{-1} . In Table 1 the calculated frequencies for glycolaldehyde are compared to the positions of observed bands from literature, and in Table 2 observed and calculated frequencies for hydroxyacetone are listed.

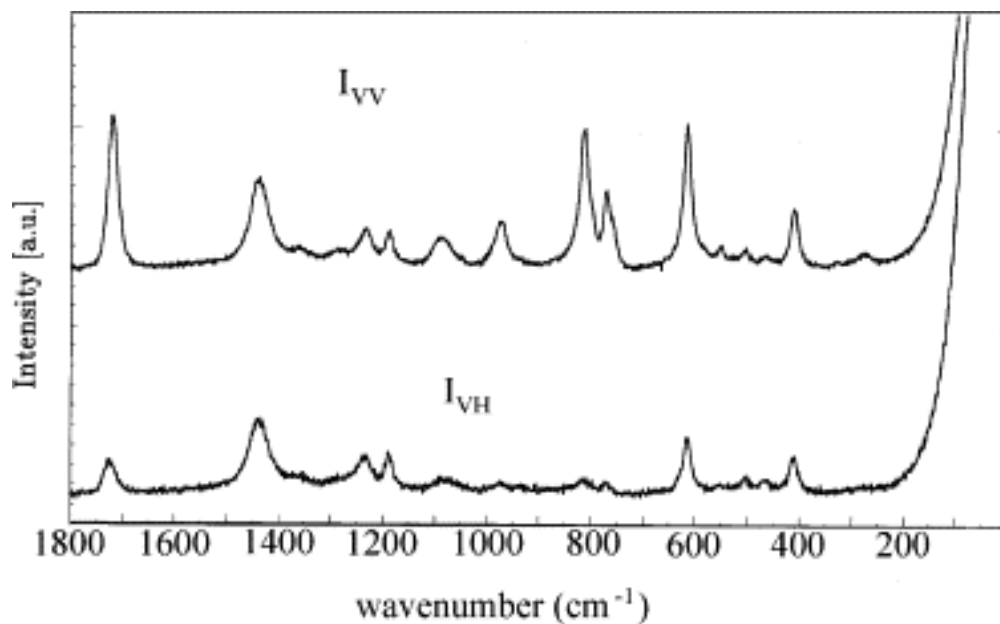


Fig 1 Polarized VV and VH Raman spectra of acetol in the $20\text{--}1800\text{ cm}^{-1}$ interval.

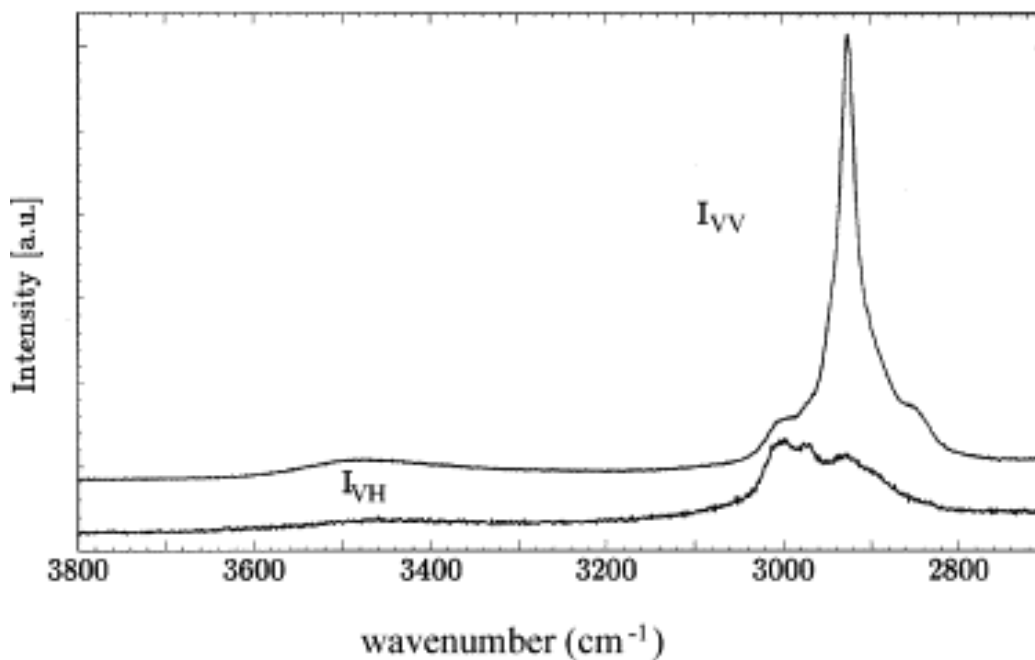


Fig 2 Polarized VV and VH Raman spectra of acetol in the $2700\text{--}3600\text{ cm}^{-1}$ interval.

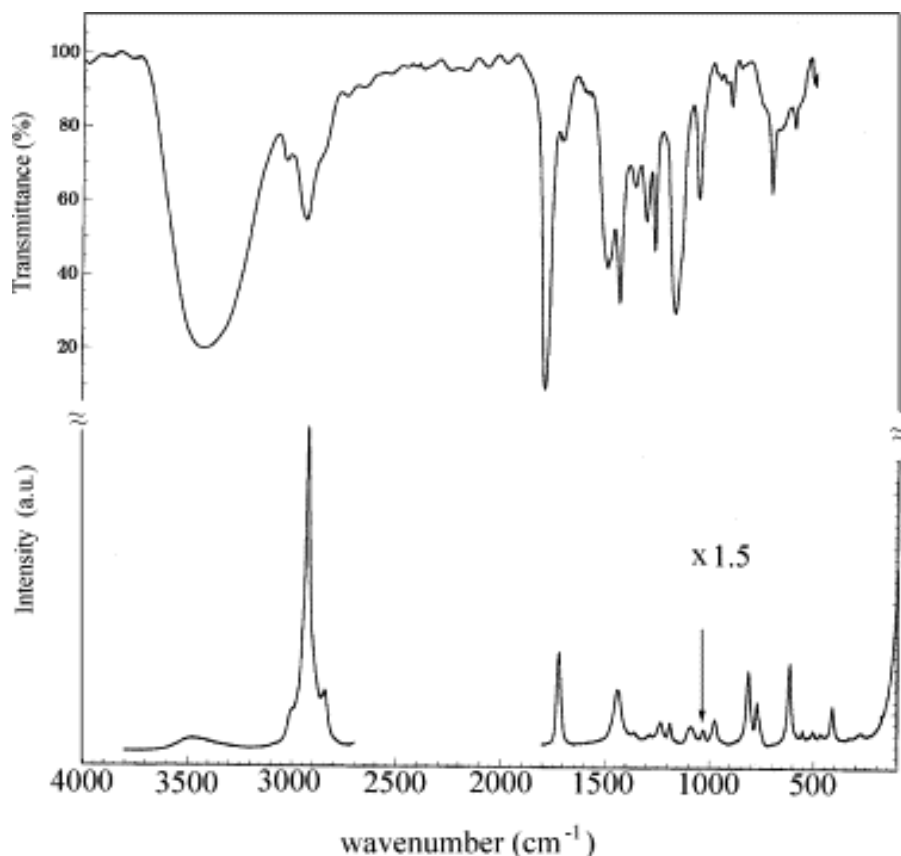


Fig 3 Infrared and Raman spectra of acetol previously warmed up in the stream of hot air for 15 min. Raman spectrum (20–1800 cm^{-1}) is multiplied by factor 1.5. The new Raman band at 1028.5 cm^{-1} is marked with an arrow.

Table 1 Observed and calculated vibrational frequencies of glycolaldehyde

Infrared vapour [13]	Infrared [14]	Ar matrix 13 K [14]	Calculated glycolaldehyde frequencies	Assignment
	Cc conformer	Tt conformer	Cc conformer	
		3668 m		
3585 m				
3565 m	3549 w		3605	O – H stretch. A'
3546 m	3541 m			
	3533 m			
2920 vw	2907 w	2940 w	2975	CH ₂ asym. stretch. A''
		2935 w		
2880 m	2895 w			
2835 s	2845 m		2893	CH ₂ sym. Stretch. A'
2810 s		2810 vw	2808	C – H stretch. A'

Infrared vapour [13]	Infrared [14] Cc conformer	Ar matrix 13 K [14] Tt conformer	Calculated glycolaldehyde frequencies Cc conformer	Assignment
	2712 w			
1764 vs				
1753 vs	1747 vs	1747 vs	1732	C – O stretch. A'
1742 vs				
	1700 m			
	1697 m			
1468 m,br				
1440 m,br	1443 w	1439 m	1422	CH ₂ scissor. A'
1410 m,br	1429 w		1367	CH ₂ def, C–O A'
	1421 w			
	1399 w			
1376 m	1367 s		1370	CH ₂ def. A''
1359 w		1353 w		
1299 w				
1282 R m				
1273 Q m				
1268 vw				
1266 m	1267 vs		1189	C – O – H bend. A'
1258 P m	1231 vw			
	1229 vw	1203 m,br		
1146 w,sh	1130 w	1129 vw		
1117 R,s	1110 vs		1043	C – O stretch. A'
1112 s				
	1107 vs			
1079 m				
1059 m		1065 vs	959	CH ₂ def. A'
1050 m			1025	CH ₂ def. A''
		998 vs		
916 w				
871 s				
861 s	858 s		876	C – C stretch. A'
859 s	855 s			C – O i.plane bend. A'
845 s				
762 w			790	C – H o.plane bend. A''
752 m	749 m			

Infrared vapour [13]	Infrared [14] Cc conformer	Ar matrix 13 K [14] Tt conformer	Calculated glycolaldehyde frequencies Cc conformer	Assignment
750 w				
748 w				
746 w				
743 w				
568 vw				
550 vw		538 w	459	O – C – C bend. A'
535 vw		535 w		
	341 vvs	331 m	396	OH torsion A''
260 ^a	274 m		188	C – H i.p. bend + C – O i.p. bend A'
195 ^a			224	CH ₂ OH torsion around C – C bond, A''

a From microwave study of Marstokk and Møllendal [22].

Table 2 Observed and calculated vibrational frequencies of hydroxyacetone

Infrared liquid acetol	Raman liquid acetol	Calculated hydroxyacetone frequencies	Assignment
3405 vs,vbr	3470 w,vbr	3605	O–H stretch. A'
2997 m	2996 w,br	3020	CH ₃ asym. stretch. A'
	2974 w,sh	3018	CH ₃ asym. stretch. A''
		2974	CH ₂ asym. stretch. A''
	2926 vs	2966	CH ₃ sym. stretch. A'
2900 s,br	2900 w,sh	2901	CH ₂ sym. stretch. A'
	2854 mw		Overtone CH ₃ bending
2809 m,sh			
1724 vs	1720 s	1751	C – O stretching A'
1641 m			Water OHO bending
1534 w			
	1435 ms,br	1459	CH ₂ scissoring A'
1422 s,br		1400	HCH bend. in CH ₃ A''
		1362	CH ₂ def. A''
1361 s	1361 w	1402	Sym. CH ₃ bend. A'
1287 m			
	1283 w,br	1394	HCH bend in CH ₂ and CH ₃ A'

Infrared liquid acetol	Raman liquid acetol	Calculated hydroxyacetone frequencies	Assignment
1233 m	1233.5 m,br	1207	COH bend. A'
1189 ms	1189.5 m	1248	CC stretch. A'
1083 s,br	1086.5 m,br	1093	CO + COH A'
1057 s,sh	1053 mw,sh		
		988	CH ₂ def. A''
973 m	975.5 m,br	982	CH ₂ def. + CO A'
888 vw			
870 vw	872 vw	873	CH ₃ rocking A''
841 w			
816 mW	813 s	864	CC str. + CH ₃ bend. A'
768 vw	771 ms	744	CH ₃ + CC + CH ₃ def. A'
750 vw	758 m,sh		
615 m	617 s	465	C – O i.p. bend + OCC bend A'
580 mw,vbr			Water libration
	552 w		
503 mw	504 w	440	C – O o.p. bend + τ_{OH} A''
	465 w		
418 mw	411 m	395	CCC bend A'
	330 w	362	τ_{OH} + C – O o.p. bend. A''
	276 w,br	242	OCC bend. + C – O i.p. bend A'
		177	τ_{CH_2OH} ^a A''
	80 ^b w,br	65	τ_{CH_3} ^a A''

a These refer to results of normal mode calculation for free molecule, the band at 80cm⁻¹ is assigned to CH₂OH torsion in hydroxyacetone solution.

b Observed in temperature reduced Raman spectrum.

Geometrical parameters needed for normal coordinate calculations were taken from microwave study of glycolaldehyde by Marstokk and Møllendal [21] and [22] and for hydroxyacetone from the microwave study by Kattija-Ari and Harmony [23]. Both molecules have the plane of symmetry in the gas phase and the calculated frequencies refer to these Cc conformers. The internal coordinates of the two molecules are depicted in Fig. 4 and Fig. 5. Force constants used in the calculation are listed in Table 3 and Table 4.

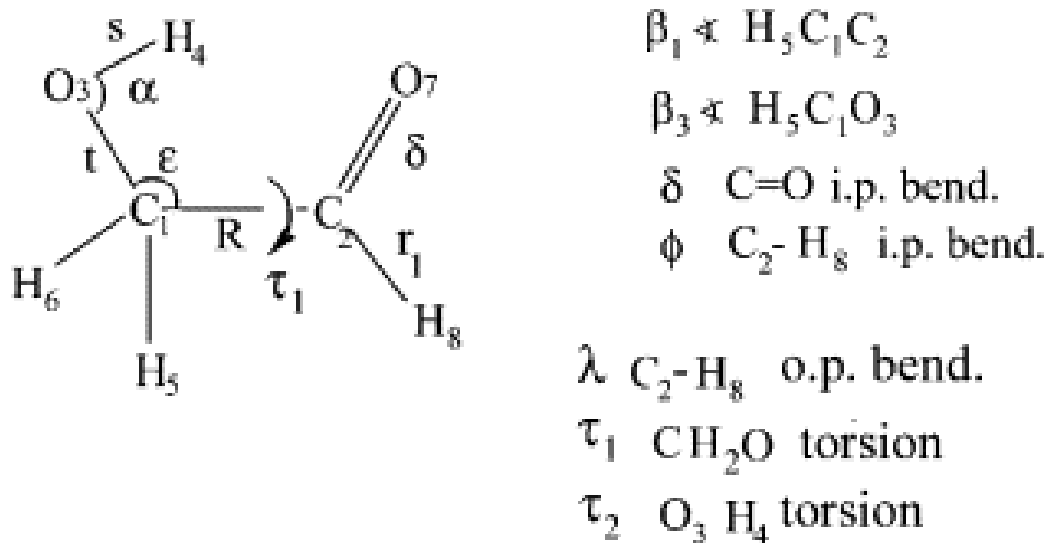


Fig 4 Definition of internal coordinates for glycolaldehyde molecule.

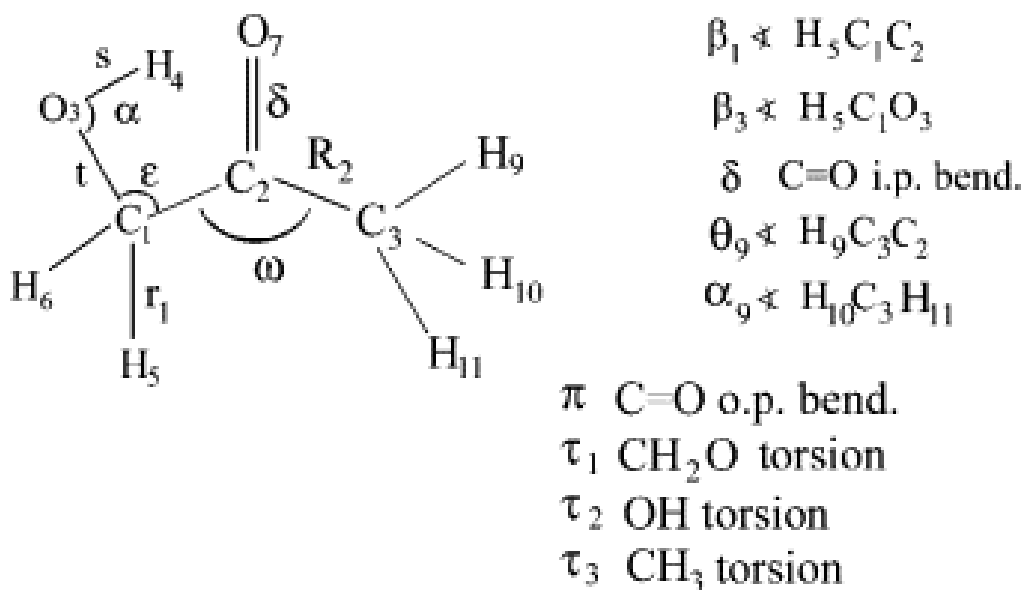


Fig 5 Definition of internal coordinates for hydroxyacetone.

Table 3 Diagonal force constants used for glycolaldehyde (GHD) and hydroxyacetone (HA) (K in N cm^{-1} , H in $10^{-16} \text{ N cm rad}^{-2}$)

Force constant	Description	Value used (GHD and HA)	Value assigned in parent molecule—if different (parent molecule, reference)
K_s	OH stretching	7.2	7.337 (EG = ethylene glycol, [25])
K_{r2}	CH ₂ stretching	4.654	(EG)

Force constant	Description	Value used (GHD and HA)	Value assigned in parent molecule—if different (parent molecule, reference)
K_{r9}	CH ₃ stretching	4.882	(acetone AN, [24])
K_{H8}	C ₂ – H ₈ str. glyc.	4.243	4.273(acetaldehyde AD, [24])
K_d	C – O stretching	10.77 and 9.9	(AN)
K_t	C – O stretching	5.044	(EG)
K_R	C – C stretching	4.760	(EG)
H_ω	C – C – C bending	1.647	(AN)
H_α	C – O – H bending	0.8	0.762 (EG)
H_ϵ	O – C – C bending	1.060	(EG)
H_β	CH ₂ bending	0.65	0.71 (EG)
H_γ	HCH bend in CH ₂	0.50	0.578 (EG)
H_θ	H – C – C bend in CH ₃	0.45	0.468 (AN)
H_α	HCH bend in CH ₃	0.49	0.521 (AN)
H_δ	O – CC in plane bend.	1.006	(EG)
$H_{\tau1}$	OH torsion	0.009	0.049 (EG)
$H_{\tau2}$	CH ₂ OH torsion	0.004	0.123 (EG)
$H_{\tau3}$	CH ₃ torsion	0.007	(AN)
H_π	C – O out of plane bend.	0.217	(AN)
H_ϕ	C ₂ – H ₈ in pl. bend.	0.435	(AD)
H_λ	C ₂ – H ₈ out of pl. bend.	0.296	(AD)

Table 4 Interaction force constants used for glycolaldehyde and hydroxyacetone (f_{rr} in N cm⁻¹, $f_{\beta,\beta}$ in 10⁻¹⁶ N cm rad⁻², and $f_{R\theta}, f_{t\phi}$ in 10⁻⁸ N rad⁻¹)

Force constant	Description	Value used	Value assigned in parent molecule—if different (parent molecule, reference)
$f_{r2,r3}$	CH ₂ stretch. inter.	-0.013	Ethylene glycol (EG, [25])
$f_{r9,r10}$	CH ₃ stretch. inter.	0.073	Acetone (AN, [24])
$f_{t,R}$	CO/CC stretch.	0.248	(EG)

Force constant	Description	Value used	Value assigned in parent molecule—if different (parent molecule, reference)
f_{β_3}, f_{β_4}	CO/ β_3 , CO/ β_4	0.076	(EG)
$f_{R,\theta}$	CC stretch., CH ₃ bend.	0.3	
$f_{\beta_1\beta_2}$	β_1/β_2	-0.168	0.068 (EG)
$f_{\beta_1\beta_3}$	β_1/β_3	0.02	-0.02 (EG)
$f_{\beta_1\beta_4}$	β_1/β_4	0.023	(EG)
$f_{\beta\varphi}$	β_1/φ	0.1	
$f_{\beta\theta_{10}}$	β_2/θ_{10}	0.1	
$f_{\theta_9,\theta_{10}}$	θ_9/θ_{10}	-0.021	(AN)

3.1. Glycolaldehyde

At present there exist differences in the assignment of glycolaldehyde bands—Michelsen and Klaboe [13] based their tentative assignment on the infrared spectrum of vapor, while Aspiala et al. [14] studied glycolaldehyde in Ar, Kr and Xe matrices by infrared spectroscopy. The greatest difference in assignment concerns O□CC in plane bending mode. In the vapour it was assigned to 859 cm⁻¹ infrared band [13], and in Ar matrix to 749 cm⁻¹ band for **Cc** conformer [14]. The band at 535 cm⁻¹ in Ar matrix was attributed to O□CC bending mode of **Tt** conformer [14]. Michelsen and Klaboe assigned the 1266 cm⁻¹ band to C□O stretching mode ($\nu(\text{CO})$) and the 1059 cm⁻¹ band to C□O□H bending ($\delta(\text{COH})$) [13], while Aspiala et al. attribute 1267 and 1110 cm⁻¹ bands in argon matrix to C□O□H bending and C□O stretching of **Cc** conformer [14]. For the other conformer present in the matrix, **Tt** conformer, $\delta(\text{COH})$ is assigned to 1203 cm⁻¹ and $\nu(\text{CO})$ to 1065 cm⁻¹ band [14]. The lowest frequency band observed in vapour was a weak band at 550 cm⁻¹, attributed to $\delta(\text{CCO})$ bending of **Cc** conformer. In argon matrix a very strong band at 341 cm⁻¹ was identified as OH torsion, and a medium band at 274 cm⁻¹ as $\delta(\text{CCO})$ of **Cc** conformer. For **Tt** conformer in Ar matrix, a weak band at 535 cm⁻¹ was taken to correspond to $\delta(\text{O□CC})$ bending mode, while $\delta(\text{CCO})$ bending mode was attributed to a medium band at 331 cm⁻¹.

Altogether there are 12 A' and 6 A'' modes belonging to C_s group that are calculated (see Table 1). The O□CC in plane bending mode is calculated at 188 cm⁻¹, which differs from the previously mentioned assignments, but is more in accord with the result from microwave study which reported the existence of a low in plane bending mode at 260 cm⁻¹ and a torsional mode at 195 cm⁻¹ [22]. The $\delta(\text{COH})$ mode was assigned to 1266 cm⁻¹ vapour band, and the $\delta(\text{CCO})$ mode to the 550 cm⁻¹ band. The strong vapour band at 861 cm⁻¹ is dominantly C□C stretching mode. Torsional transitions were calculated at 396 cm⁻¹ (τOH) and 224 cm⁻¹ ($\tau\text{CH}_2\text{O}$).

3.2. Hydroxyacetone

Hydroxyacetone is extremely hygroscopic substance. In a few days there is so much water absorbed from the air, that the intensity ratio of 1740 and 1643 cm^{-1} infrared bands changes from 10 to 2 suggesting the increase of water content from 10 to 50%. Also, there is a high fluorescence emanating from the substance when illuminated with 514.5 nm laser light. One needs to wait for several hours before the system relaxed into the ground state and the level of background signal dropped enough for Raman spectra to be acquired. At low temperatures the fluorescent background signal could not be eliminated.

The results of normal mode calculation for 17 A' and 10 A'' vibrations of the **Cc** conformer are given in Table 2. For the majority of high frequency bands, the calculated values agree more or less with those of the corresponding glycolaldehyde conformer. The bands corresponding to COH bending and C=O stretching mode lie at 30 cm^{-1} lower wavenumbers than in glycolaldehyde, but the calculated value for C=O stretching is higher for glycolaldehyde than for hydroxyacetone. There are two bands both in infrared (1083 and 1057 cm^{-1}) and in Raman spectrum (1086.5 and 1053 cm^{-1}) that are assigned to $\nu(\text{C=O})$, and this is one of the indicators of several hydroxyacetone conformers in the solution.

The broad water libration band observed at $\sim 500 \text{ cm}^{-1}$ in the infrared spectrum overlaps with the lower frequency acetol bands: C=O in plane bending, CCC bending, C=O out of plane bending, OCC bending and hydroxyl torsion. The in plane C=O bending mode is observed at 617 cm^{-1} in Raman and at 615 cm^{-1} in the infrared spectrum of liquid acetol, while the C=O out of plane bending mode is attributed to 503 cm^{-1} infrared and 504 cm^{-1} Raman band. The CCC bending mode is assigned to 418 cm^{-1} infrared and 411 cm^{-1} Raman band (in acetone it is 483 cm^{-1}). Torsion of the hydroxyl group is calculated at 362 cm^{-1} and taken to correspond to a weak Raman band centered at 330 cm^{-1} . The OCC in plane bending mode is calculated to be 242 cm^{-1} and assigned to broad and weak 270 cm^{-1} Raman band.

Of the two lowest internal modes, CH_2OH torsion and CH_3 torsion, only one seems to be observed at 80 cm^{-1} in Raman spectra of acetol (see Fig. 6 and Fig. 7). The low frequency Raman spectrum of liquid was divided by temperature dependent factor contributing to Raman scattered intensity [30]:

$$(\omega_0 - \omega_i)^4 \omega_i^{-1} \left(1 - \exp \left(-\frac{h\omega_i c}{kT} \right) \right), B_{\text{CH}_3}$$

where ω_0 is the absolute frequency (in wavenumbers), ω_i the Raman shift, h the Planck's constant, and k the Boltzmann's constant. The resulting intensity function is usually denoted $R(\omega)$. Methyl libration bands are notoriously weak in Raman spectra [34], therefore the 80 cm^{-1} band is attributed to hydroxymethyl torsions.

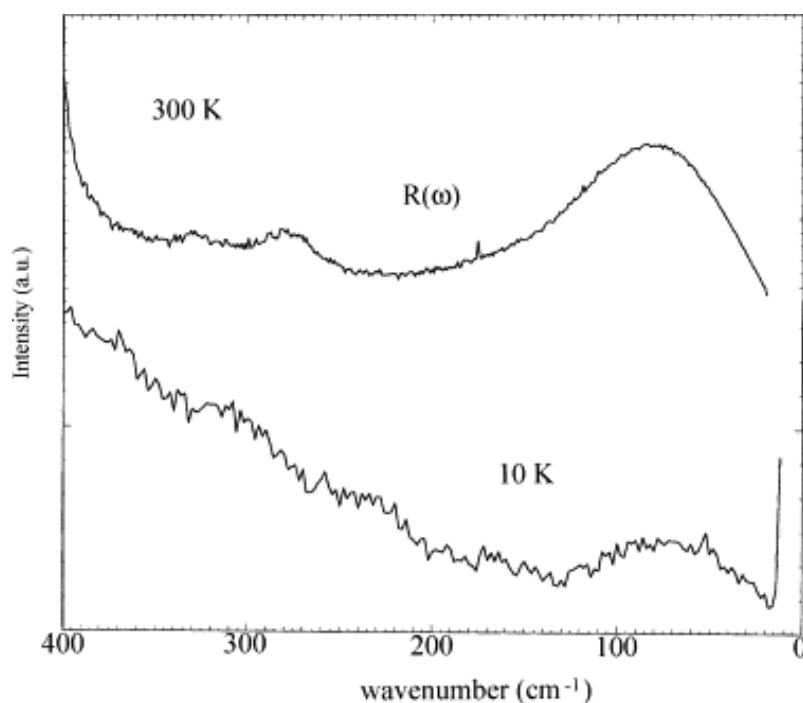


Fig 7 Temperature reduced Raman spectrum $R(\omega)$ of acetol at room temperature (300 K) (see text for an explanation), and low frequency Raman spectrum for a solid at 10 K.

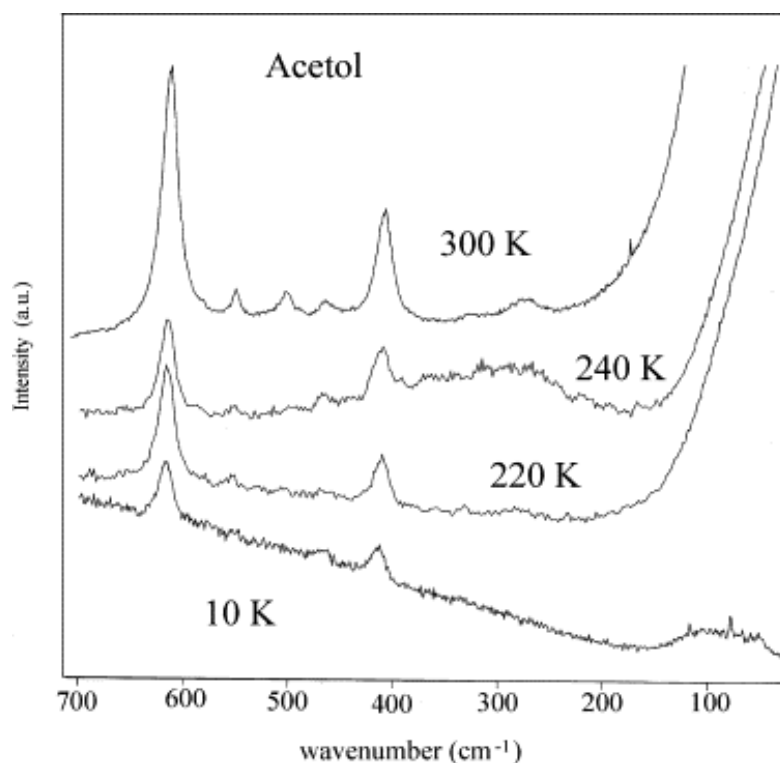


Fig 1 Temperature dependence of low frequency Raman spectra of acetol (20–700 cm^{-1}).

There are still two unassigned Raman bands of acetol: one at 465 cm^{-1} and the other at 552 cm^{-1} .

4. Discussion

It was pointed out [23] that the barrier to methyl group rotation in hydroxyacetone is significantly lower (it is 810 J mol^{-1}) than in other similar compounds such as acetone or acetaldehyde where it is 3260 and 4890 J mol^{-1} [23]. The explanation lies probably in the existence of intramolecular hydrogen bond, which causes the shift of electron density from the carbonyl group to the O...H bond [23]. Taking the internal rotation constant B_{CH_3} of methyl group equal to 5.58 cm^{-1} , with the barrier height V_3 equal to 67.5 cm^{-1} , than $0A \rightarrow 1A$ transition of methyl group lies at 67.5 cm^{-1} (calculated by VIBAR [29]).

As far as OH torsion in the free molecule is concerned, Aspiala et al. [14] estimated from the ab initio calculations that the barrier would be around 3 kJ mol^{-1} (250 cm^{-1}). In the internal axis approximation, the B_{OH} is 16.18 cm^{-1} ; with the barrier height V_1 equal to 250 cm^{-1} , the $0+ \rightarrow 1+$ transition is calculated equal to 113.5 cm^{-1} .

Since we do not have any spectra of pure hydroxyacetone, we compare these results with the information available for similar compounds and with the low frequency Raman spectra of water solution of hydroxyacetone (Fig. 6). At room temperature, the temperature reduced spectrum $R(\omega)$ is shown [30], while the spectrum at 10 K corresponds to a glassy state. In both cases there is a broad low frequency Raman mode at $\sim 80 \text{ cm}^{-1}$. In ethanol, OH and CH_2OH internal rotations are strongly coupled, and the two infrared vapour bands at 250 and 305.5 cm^{-1} interpreted as torsional transitions [31] and [32]. In ethylene glycol, $\text{CH}_2\text{OHCH}_2\text{OH}$, there are three internal rotations present. Frei et al. observed OH torsions at 361 and 268 cm^{-1} in Ar matrix, and CH_2OH torsion at 212 cm^{-1} in Xe matrix by infrared spectroscopy [33]. For the same molecule, Takeuchi and Tasumi observed infrared-induced rotamerization and assigned the OH torsional transitions to bands above 300 cm^{-1} while the CH_2OH torsion was calculated to lie around 145 cm^{-1} for all conformers [25]. In glycolaldehyde the OH torsion is at 341 cm^{-1} [14] and the hydroxymethyl torsion at 195 cm^{-1} [22].

Bearing in mind the hydroxyl group dynamics in similar compounds discussed above, it seems probable that the broad low frequency Raman band at 80 cm^{-1} corresponds to CH_2OH torsions in water solution of hydroxyacetone. As far as OH torsion is concerned, it is assigned to a weak 330 cm^{-1} Raman band which gains the intensity at 240 K and disappears on further cooling (see Fig. 7). The CH_3 internal rotation transitions were not observed.

The unassigned 465 and 552 cm^{-1} Raman bands are probably skeletal bending bands (corresponding to OCC bending modes) of some other conformer. Also, there are two strong bands at 1083 and 1057 cm^{-1} in the infrared spectrum, corresponding to C=O stretching vibrations, supporting the hypothesis of at least two conformers existing in the solution.

5. Conclusion

Vibrational assignment of hydroxyacetone was done by comparing the results of semi-empirical valence force field calculation (based on acetone, acetaldehyde and ethylene glycol and tested on glycolaldehyde) with Raman and infrared bands of 90 wt.% water solution of hydroxyacetone. The C=O in plane bending mode was assigned to 615 cm^{-1} infrared and 617 cm^{-1} Raman band, the C=O out of plane mode to 503 cm^{-1} infrared and 504 cm^{-1} Raman band, the OCC bending to 276 cm^{-1} Raman band, and the CCC bending to 411 cm^{-1} Raman band. The hydroxymethyl group internal rotation transitions were observed in Raman spectrum of liquid and glass (below 150 K) as a broad band centered around 80 cm^{-1} , while the OH torsion is assigned to a weak and broad Raman band at 330 cm^{-1} .

Two strong infrared bands at 1083 and 1057 cm^{-1} instead of one in the region of C=O stretching vibration indicate the presence of more than one conformer in the 90 wt.% solution of hydroxyacetone in water. The shifting of the particularly temperature sensitive Raman band from 1053 to 1028.5 cm^{-1} on warming of the sample is explained as the change of hydrogen bonding in one of the conformers. The band at 1053 cm^{-1} is dominantly a C=O stretching mode, mixed with COH bending. It is via the bending mode that the hydrogen bonding manifests itself so sharply.

Also, in Raman spectrum there are two additional bands, at 465 and 552 cm^{-1} , which are assigned to skeletal deformations of the second conformer. The NMR and UV results on diluted acetol state that hydroxyacetone is 96% in the carbonyl form and only up to 4% in the hydrated form [20]. The results presented here give evidence of at least two conformers of hydroxyacetone in the carbonyl form exist in the 90 wt.% water solution.

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